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Investigation of Low Resistance Contacts to Pb-Sb-Ag-Te (LAST) Materials for Module Fabrication

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ABSTRACT

Low electrical contact resistance is essential for the fabrication of high efficiency thermoelectric generators. These contacts must be stable to high temperatures and through thermal cycling. Here we present the fabrication procedure and characterization of several contacts to Pb-Sb-Ag-Te (LAST) compounds. Contact materials investigated include tungsten, antimony, tin, nickel, and a bismuth antimony based solder. The contacts were typically deposited by an electron beam evaporation method after careful preparation of the sample surface. The resistances were measured by using the transmission line model (TLM), and ohmic behavior was verified through current vs. voltage measurements. The best contact resistivities of less than 20 $\mu\Omega\cdot cm^2$ have been measured for annealed antimony to n-type LAST samples. We present these procedures for fabricating low resistance contacts and the use of these contact materials toward the fabrication of high efficiency thermoelectric generator modules.

INTRODUCTION

Contact resistance can significantly degrade the performance of thermoelectric generators [1]. In an effort to minimize this loss, we have begun investigations of contact resistance measurements and the characterization of contacts between Pb-Sb-Ag-Te (LAST) or Pb-Sb-Ag-Te-Sn (LASTT) materials and various metals and alloys. Diffusion bonding techniques and procedures are also presented.

EXPERIMENTAL PROCEDURE

We have investigated the e-beam deposition of various metals onto LAST and LASTT materials in an appropriate pattern for transmission line model measurements of contact resistivity [2]. By measuring the resistance between multiple contact pads with varying spacings, a plot of the resistance vs. contact spacing can be made where a linear extrapolation to the zero spacing results in two times the contact resistance, $2R_c$. Figure 1 shows the typical pattern used.

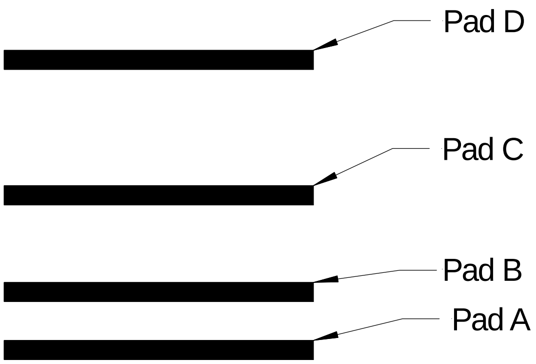


Figure 1. Typical pattern for depositing contacts for the TLM measurement technique.

Each contact pad is approximately 0.5mm in length, and the width of the contact extends across the width of the sample. By extending the contact across the sample width, errors due to current crowding are minimized. Each contact was e-beam deposited to a thickness ranging from 100nm to 1micron as measured by a quartz crystal monitor during deposition. The system is pumped down to a vacuum level of around 4×10^{-6} Torr. This method is an excellent way of depositing thin films anywhere from nanometers thick to even a micron, and was found to work well even for tungsten. Table 1 summarizes the results obtained for various material contacts to LAST (n-type) and LASTT (p-type) materials. The results show low resistance contacts are possible through this deposition technique. For the lowest resistance contacts, Sb on LAST, the contacts were also annealed at 425 ºC for approximately 40 hours, before measuring the contact resistance.

Table 1. Summary of Contact Materials Investigated.

N/P LAST	Material	E-Beam Voltage	E-Beam Current	Deposited Material Thickness	Contact Resistance ($\mu\Omega cm^2$)
P	Sb	9kV	5mA	1μm	80
N	Sb	9kV	5mA	1μm	20
P	Ag	9kV	200mA	500nm	500
N	Ag	9kV	200mA	500nm	1800
N	Cr	9kV	150mA	500nm	275
P	Cr	9kV	150mA	500nm	120
N	Ti	9kV	250mA	250nm	130
P	Ti	9kV	250mA	250nm	145
P	W	9kV	400mA	100nm	65
P	W/Ag	9kV	400/200mA	20nm/200nm	140

Tungsten has been reported to provide low resistance contacts to PbTe [3].

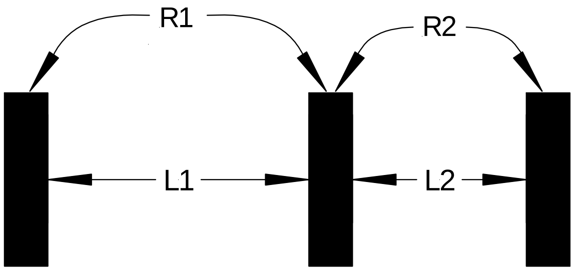


Figure 2. Resistance, and spacing measurements for the TLM.

For a uniform sample, the measured resistance, R1 or R2 in Figure 2, linearly increase with increasing distance between contacts. For both R1 and for R2, the measured value includes two contact resistances such that the contact resistance can be determined by

$$R_c = \frac{R_2 \cdot l_1 - R_1 \cdot l_2}{2(l_1 - l_2)} \tag{1}$$

This calculation has been shown to give accurate measurements to low contact resistances [2]. Contact resistivities of less than 20 $\mu\Omega\cdot cm^2$ have been measured for annealed antimony to n-type LAST samples. The sample was annealed at 425ºC for 39.5 hours. Since these results were promising, we investigated diffusion bonding between LAST and metal interconnects (Ni), using antimony as the bonding agent.

DIFFUSION BONDING

Diffusion bonding is a technique of bonding two similar or dissimilar metals, alloys, or nonmetals [4]. This is achieved by pressing the two materials that you would like to be bonded, preferably under vacuum or in the presence of an inert gas to reduce oxidization. The three factors that control the how well the bond is formed are the temperature you are bonding at, the amount of weight is placed onto the samples during bonding, and lastly is the amount of time one stays at the bonding temperature.

The bonding temperature should be anywhere to 50%-70% of the melting point of the most fusible metal. The temperature aids in the inter-diffusion of the atoms across the interface. The bonding pressure first forces contact between the two materials but also fills voids and push out any oxides that may reside on either of the two interfaces. For high temperature bonding, time is an important factor and should be minimized. If the bonding time is too long, voids can form at the interfaces, and more importantly, chemical changes of the materials can occur.

EPERIMENTAL TECHNIQUE

For the diffusion bonding process a furnace system was designed and assembled with a rough pump and inert gas (argon, Ar_2) backfill capabilities. The samples were placed into a quartz boat designed to hold up to 120 unicouples at once. An optional quartz weight can be placed on each sample to aid in the diffusion process. The sample boat was then placed into the center of the furnace with a push rod. All apertures are then sealed and vacuum is pulled for more than an hour. After the vacuum reaches 20~15mTorr, argon flow into the furnace was initiated. The pressure was monitored and allowed to rise in the tube to 150-200Torr. After pressure stabilization, the temperature was set to the desired bonding temperature which typically takes 10-15 minutes to reach a set point of 600°C. Once the desired bonding temperature is reached, the furnace is set back to room temperature and allowed to cool naturally. After cooling, the quartz tube chamber is then pumped down again, vented to atmosphere, and the samples are retrieved from the furnace. The following table is a list of diffusion bonds that were investigated.

Table 2. Investigated diffusion bonds.

Bond Investigated to LAST	Temp (°C)/ Time (min)	Pressure Ar_2	Visual Inspection
$ZnCl_2$ pre-etch + Sb powder	650/10	300mTorr	No Bond (out- gassing)
Sb	622/10	29Torr	Good Bonds (no out-gassing)
Bi/Sb (55/45) on Ni	500/10	200Torr	No Bonds
Bi/Sb only	500/10	300Torr	Good Bonds
Bi/Sb to Ni (No LAST)	500/10	300Torr	Bi/Sb blackens on Ni
Sb only	604/10	200Torr	Good bonds
Sb on Ni (No LAST)	604/10	200Torr	Not Bad- a little blackening
Bi/Sb (55/45) on Ti (No LAST)	500/10	215Torr	Good bond between metals
Bi/Sb (55/45) on W (No LAST)	500/10	215Torr	No bond between metals
In (0.5mm thick) on Ni	640/10	215Torr	Consumed Samples
In on Ni (No LAST)	500/10	215Torr	Good Bond between Metals
In on Ni (prealloyed)	650/10	580Torr	Good Bond
In 1μm thick on Ni	640/10	450Torr	Good Bond
Stainless steel	755/240	250Torr	Well Bonded

BOND MEASUREMENTS

For bonds made to the legs to be used in the fabrication of modules, the contacts are made to the ends of the sample. Under these conditions, the contact resistance can be measured by scanning across the junction while alternating current is used to monitor the resistance. Initial measurements where an antimony plate was used to bond to p-type leg of LASTT is shown in Figure 3. This suggests that the plasma etching step used in the deposition of materials for the TLM measurements was very important for low resistance contacts. Some low resistance bonds were formed by the direct bonding procedure as shown in Figure 4, and Figure 5, where a direct bond between LASTT and Bi_2Te_3 was found to show low contact resistance. This could be very advantageous for segmented leg configurations.

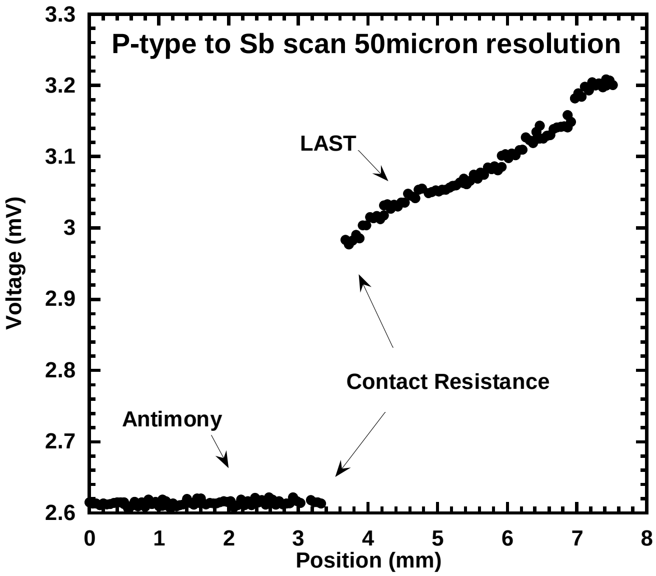


Figure 3. Measurement along sample of high resistance bond between Sb and LASTT.

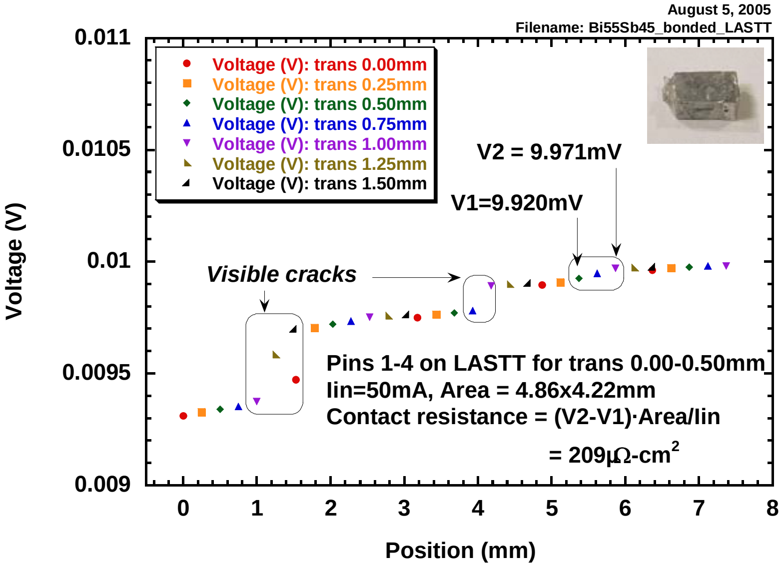
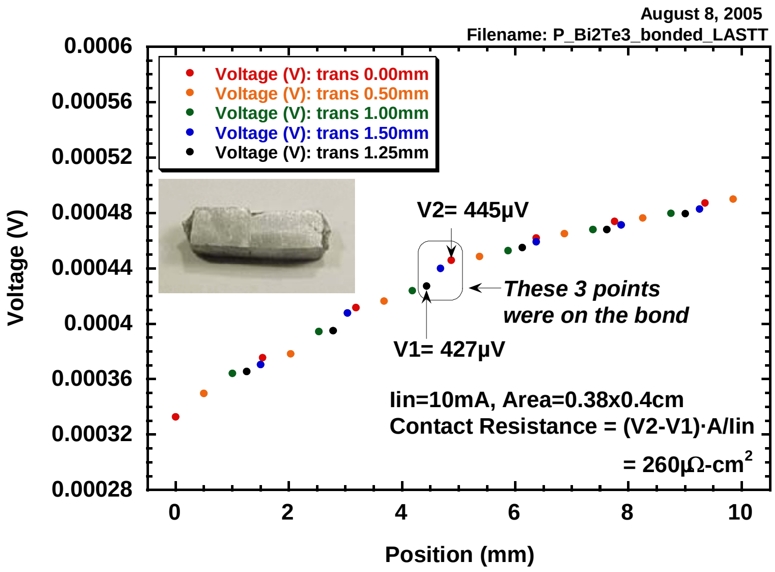


Figure 4. Voltage sweep across cracks on the sample (LASTT) and across a bond to $Bi_{55}Sb_{45}$.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Filename: P_Bi2Te3_bonded_LASTT

Figure 5. Low contact resistance between a Bi_2Te_3 and LASTT.

CONCLUSIONS

Low resistance contacts have been made to LAST and LASTT materials through plasma etching followed by e-beam deposition and annealing of several promising contact metals including Sb, Cr, and Ti. Further studies of diffusion bonding of Sb to LAST and LASTT suggest that plasma cleaning of the surfaces and in vacuum deposition of the contacts helps to reduce the contact resistance. The TLM technique and scanning probe method were utilized in characterizing the contacts formed. Direct bonding of Bi_2Te_3 to LASTT has also shown to give relatively low contact resistance.

ACKNOWLEDGEMENT

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